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XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON SUBSTITUTED PYROMUCIC ACIDS.

SECOND PAPER.

By Henry B. Hill and Arthur W. Palmer.

Presented March 14, 1888.

ON SULPHOPYROMUCIC ACIDS.*

Pyromucic acid shows in many of its reactions so close an analogy to benzoic acid that a study of its behavior toward concentrated sulphuric acid could hardly fail to yield interesting results. In 1860 Schwanert † prepared a sulphopyromucic acid by distilling sulphuric anhydride slowly over powdered pyromucic acid. The barium salt was said to be not distinctly crystalline, and its composition was established by a single determination of barium in the salt dried at 150°. With the exception of the brief notice by Schwanert, we have been able to find no mention of furfuran derivatives containing the sulpho-group. We have found that a sulphopyromucic acid is formed without difficulty when pyromucic acid is dissolved in fuming sulphuric acid, and that a second sulphonic acid may readily be made by indirect methods. We have also prepared and studied several derivatives of these sulphonic acids containing bromine, and have succeeded in establishing the constitution of these various products.

δ-Sulphopyromucic Acid.

If dry pyromucic acid is slowly added to fuming sulphuric acid (Sp. Gr.1. 95), it dissolves without serious discoloration, and in a short

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* A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University in May, 1886, by Arthur W. Palmer, then candidate for the degree of Doctor of Science.

† Annalen d. Chem. u. Pharm., cxvi. 268.

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time the formation of the sulphonic acid is complete. We have usually taken three parts of sulphuric acid to one of pyromucic, and have allowed the viscous solution to stand for twenty-four hours before diluting and neutralizing with baric carbonate. The aqueous solution filtered from the baric sulphate and concentrated by evaporation deposits on cooling globular aggregations of minute crystals, which are readily purified by recrystallization from hot water. The acid prepared by exact precipitation with sulphuric acid is extremely soluble in water, but may be obtained by concentration in large transparent prisms which deliquesce in moist air.

Baric δ-Sulphopyromucate, $BaC_5H_2SO_6 . 4 H_2O$. — This salt crystallizes in thin flat prisms, which are usually closely aggregated in hemispherical masses. It is readily soluble in hot water, more sparingly soluble in cold water, and its aqueous solution is precipitated by the addition of alcohol. When dried by exposure to the air it contains four molecules of water, a part of which it slowly loses over sulphuric acid or at 100°, the rest at 160°.

I. 2.1205 grm. of the air-dried salt lost, at 162°, 0.3827 grm. H_2O.
II. 2.5754 grm. of the air-dried salt lost, at 160°, 0.4605 grm. H_2O.

	Calculated for	Found.	
	$BaC_5H_2SO_6 . 4 H_2O$.	I.	II.
H_2O	18.02	18.05	17.88

I. 0.7695 grm. of the salt dried at 160° gave 0.5480 grm. $BaSO_4$.
II. 0.7010 grm. of the salt dried at 160° gave 0.4990 grm. $BaSO_4$.

	Calculated for	Found.	
	$BaC_5H_2SO_6$.	I.	II.
Ba	41.90	41.87	41.85

The solubility of the salt in cold water we have determined according to the method of V. Meyer.

I. 15.1350 grm. of a solution saturated at 21° gave 0.3672 grm. $BaSO_4$.
II. 13.9856 grm. of a solution saturated at 21° gave 0.3384 grm. $BaSO_4$.

The aqueous solution saturated at 21° therefore contained the following percentages of the anhydrous salt: —

I.	II.
3.40	3.39

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Acid Baric δ-Sulphopyromucate, $Ba(C_5H_3SO_6)_2 . 4 H_2O$ and $6 H_2O$.— Although this salt may be formed by the action of hydrochloric acid upon the neutral salt, its ready solubility in cold water makes it more conveniently prepared from equivalent quantities of the free acid and the neutral salt. On cooling the concentrated solution, the salt separates in long slender prisms containing six molecules of water. From more dilute solutions, when crystallization begins at ordinary temperatures, the salt separates in well-formed rhombic plates which contain four molecules of water. Not unfrequently both forms appear together, and we have not been able to determine with precision the conditions essential to the formation of either. The long slender prisms effloresce slowly when exposed to the air. When dried by pressure and by short exposure to the air, it gave the following results: —

I. 0.6298 grm. of the salt lost, at 100°, 0.1056 grm. H_2O.
II. 1.7845 grm. of the salt lost, at 120°, 0.3055 grm. H_2O.

	Calculated for $Ba(C_5H_3SO_6)_2 . 6 H_2O$	Found. I.	II.
H_2O	17.22	16.77	17.12

I. 0.5242 grm. of the salt dried at 100° gave 0.2361 grm. $BaSO_4$.
II. 0.7035 grm. of the salt dried at 120° gave 0.3155 grm. $BaSO_4$.
III. 0.7629 grm. of the salt dried at 120° gave 0.3420 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	Found I.	II.	III.
Ba	26.39	26.48	26.36	26.35

The rhombic plates did not lose in weight when exposed to the air, and but slowly over sulphuric acid. The air-dried salt gave the following results: —

I. 4.3735 grm. of the air-dried salt lost, at 105°, 0.5235 grm. H_2O.
II. 1.4496 grm. of the air-dried salt lost, at 105°, 0.1762 grm. H_2O.
III. 1.6332 grm. of the air-dried salt lost, at 135°, 0.2010 grm. H_2O.

	Calculated for $Ba(C_5H_3SO_6)_2 . 4 H_2O$.	Found. I.	II.	III.
H_2O	12.18	11.97	12.16	12.31

I. 0.6969 grm. of the salt dried at 105° gave 0.3125 grm. $BaSO_4$.
II. 0.6325 grm. of the salt dried at 140° gave 0.2825 grm. $BaSO_4$.
III. 0.5982 grm. of the salt dried at 140° gave 0.2682 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	Found. I.	II.	III.
Ba	26.39	26.36	26.26	26.36

Calcic δ-Sulphopyromucate, $CaC_5H_2SO_6 . 3 H_2O$. — This salt is quite soluble in cold water, and crystallizes in flat concentrically grouped prisms, which slowly effloresce over sulphuric acid.

0.7413 grm. of the salt lost, at 130°, 0.1364 grm. H_2O.

	Calculated for $CaC_5H_2SO_6 . 3 H_2O$.	Found.
H_2O	19.01	18.40

I. 0.5737 grm. of the salt dried at 125° gave 0.3383 grm. $CaSO_4$.
II. 0.6405 grm. of the salt dried at 125° gave 0.3770 grm. $CaSO_4$.

	Calculated for $CaC_5H_2SO_6$.	Found.	
		I.	II.
Ca	17.40	17.34	17.31

Plumbic δ-Sulphopyromucate, $PbC_5H_2SO_6 . 2 H_2O$. — This salt is readily soluble in hot water, more sparingly in cold, and crystallizes in clustered needles. The air-dried salt contained two molecules of water.

2.1320 grm. of the air-dried salt lost at 105° 0.1805 grm. H_2O.

	Calculated for $PbC_5H_2SO_6 . 2 H_2O$.	Found.
H_2O	8.31	8.47

I. 0.6682 grm. of the salt dried at 110° gave 0.5085 grm. $PbSO_4$.
II. 0.5046 grm. of the salt dried at 110° gave 0.3837 grm. $PbSO_4$.
III. 1.0150 grm. of the salt dried at 110° gave 0.5570 grm. CO_2 and 0.0660 grm. H_2O.

	Calculated for $PbC_5H_2SO_6$.	Found.		
		I.	II.	III.
Pb	52.14	51.99	51.96	
C	15.16			14.97
H	0.50			0.72

Argentic δ-Sulphopyromucate, $Ag_2C_5H_2SO_6$. — The silver salt is sparingly soluble in cold water, somewhat more readily soluble in hot water, and crystallizes in short thick prisms. The air-dried salt lost slightly in weight when heated at 120°, but the loss was insignificant.

I. 0.6788 grm. of the salt gave 0.4779 grm. AgCl and 0.3923 grm. $BaSO_4$.
II. 0.5255 grm. of the salt gave 0.3703 grm. AgCl and 0.3028 grm. $BaSO_4$.

	Calculated for $Ag_2C_5H_2SO_6$	Found. I.	II.
Ag	53.21	53.01	53.04
SO_3	19.97	19.85	19.78

Potassic δ-Sulphopyromucate, $K_2C_5H_2SO_6 \cdot 4\,H_2O$. The potassium salt is extremely soluble even in cold water, and crystallizes in long slender prisms, which apparently contain four molecules of water. They effloresce quite rapidly when exposed to the air, and our determinations of the water of crystallization are, therefore, not entirely satisfactory.

I. 2.4108 grm. of the salt dried by short exposure to the air lost, at 135°, 0.4966 grm. H_2O.
II. 0.9701 grm. of the salt dried by pressure only lost, at 100°, 0.2074 grm. H_2O.
III. 1.3420 grm. of the salt dried by short exposure to the air lost, at 115°, 0.2775 grm. H_2O.

	Calculated for $K_2C_5H_2SO_6 \cdot 4\,H_2O$.	Found. I.	II.	III.
H_2O	21.15	20.60	21.38	20.68

I. 0.5573 grm. of the anhydrous salt gave 0.3608 grm. K_2SO_4.
II. 0.5035 grm. of the anhydrous salt gave 0.3242 grm. K_2SO_4.

	Calculated for $K_2C_5H_2SO_6$.	Found. I.	II.
K	29.16	29.07	28.91

Acid Potassic δ-Sulphopyromucate, $KC_5H_3SO_6$. — The acid potassium salt is very soluble in water, and crystallizes in large anhydrous prisms.

I. 0.8655 grm. of the salt gave 0.3253 grm. K_2SO_4.
II. 0.8290 grm. of the salt gave 0.3127 grm. K_2SO_4.
III. 0.7694 grm. of the salt gave 0.2879 grm. K_2SO_4.

	Calculated for $KC_5H_3SO_6$.	Found. I.	II.	III.
K	16.99	16.89	16.93	16.81

Sodic δ-Sulphopyromucate, $Na_2C_5H_2SO_6 \cdot 5\,H_2O$. — The neutral sodium salt is extremely soluble in water, and crystallizes in long slender needles, which appear to contain five molecules of water. The same salt is obtained in the form of fine felted needles by crystallization from dilute alcohol.

I. 1.5082 grm. of the salt dried by short exposure to the air lost, at 110°, 0.3970 grm. H_2O.
II. 1.4198 grm. of the salt recrystallized from dilute alcohol and dried by short exposure to the air lost, at 135°, 0.3773 grm. H_2O.
III. 1.0232 grm. of the salt recrystallized from dilute alcohol and dried by pressure only lost, at 135°, 0.2785 grm. H_2O.

	Calculated for $Na_2C_5H_2SO_6 . 5 H_2O$.	Found.		
		I.	II.	III.
H_2O	27.61	26.32	26.57	27.22

I. 0.5195 grm. of the salt dried at 110° gave 0.3115 grm. Na_2SO_4.
II. 0.5592 grm. of the salt dried at 110° gave 0.3357 grm. Na_2SO_4.

	Calculated for $Na_2C_5H_2SO_6$.	Found.	
		I.	II.
Na	19.49	19.43	19.45

Acid Sodic δ-Sulphopyromucate, $NaC_5H_3SO_6 . H_2O$. — This salt crystallizes in long slender prisms, which do not lose in weight when exposed to the air or over sulphuric acid.

I. 2.1303 grm. of the air-dried salt lost, at 110°, 0.1658 grm. H_2O.

	Calculated for $NaC_5H_3SO_6 . H_2O$.	Found.
H_2O	7.76	7.78

I. 1.0224 grm. of the salt dried at 110° gave 0.3371 grm. Na_2SO_4.
II. 0.9498 grm. of the salt dried at 110° gave 0.3154 grm. Na_2SO_4.

	Calculated for $NaC_5H_3SO_6$.	Found.	
		I.	II.
Na	10.75	10.69	10.76

δ-Sulphopyromucamide, $C_5H_2SO_4(NH_2)_2$. — By acting upon the dry sodium salt of δ-sulphopyromucic acid with phosphoric pentachloride, and expelling at a gentle heat the greater part of the phosphoric oxychloride formed in the reaction, a viscous oil was obtained which did not invite further investigation. It was, therefore, at once converted into the corresponding amide by the action of concentrated ammonic hydrate. The product of the reaction, after recrystallization from boiling water, formed long flat prisms readily soluble in hot water, sparingly soluble in cold water, which melted at 213°.

I. 0.3441 grm. of substance gave 47.2 c.c. moist nitrogen at 27° and under a pressure of 763 mm.
II. 0.2025 grm. of substance gave 0.2507 grm. $BaSO_4$.

	Calculated for $C_5H_2SO_4(NH_2)_2$.	Found. I.	Found. II.
N	14.73	15.18	
S	16.84		17.00

Action of Bromine.

At ordinary temperatures dry bromine has little or no action upon dry δ-sulphopyromucic acid. At 100° in sealed tube a complicated reaction ensues, which we have not yet fully investigated. Ordinary dibromsuccinic acid is formed in considerable quantity, and at the same time a small amount of mucobromylbromide, as was shown by the blue color developed in alkaline solution, and by the formation of mucobromic acid melting at 120–121° on heating with water. There was also formed in small quantity a beautifully crystalline substance, sparingly soluble even in boiling alcohol, which contained sulphur, but no bromine. This substance we unfortunately have not yet succeeded in obtaining in quantity sufficient for further study.

In aqueous solution bromine rapidly oxidizes δ-sulphopyromucic acid, even in the cold. The final product of the reaction is fumaric acid, and we have hitherto been unable to isolate any intermediate products. It is probable, however, that maleic acid is in fact the first product of the oxidation. If bromine be added to an aqueous solution of the barium salt of the acid, baric sulphate is immediately thrown down; but since the amount of baric sulphate thus formed is slightly less than the theoretical quantity, secondary products containing sulphur are doubtless formed. In the complete oxidation of the acid we have used a slight excess of bromine, and have finished the reaction by gentle heat. The fumaric acid obtained was identified by qualitative tests, and by the analysis of the silver salt.

I. 0.2124 grm. of the salt dried at 120° gave 0.2406 grm. AgBr.
II. 0.2056 grm. of the salt dried at 120° gave 0.2332 grm. AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found. I.	Found. II.
Ag	65.46	65.07	65.15

The decomposition with bromine, therefore, takes place in great part according to the equation,

$$C_5H_4SO_6 + 3\ Br_2 + 4\ H_2O = C_4H_4O_4 + CO_2 + H_2SO_4 + 6\ HBr.$$

Action of Nitric Acid.

The oxidation of δ-sulphopyromucic acid with dilute nitric acid takes place but slowly, and even after long boiling with moderately concentrated acid the decomposition is far from complete. After boiling for some time with acid of Sp. Gr. 1.20, and evaporation upon the water-bath, fumaric acid was obtained, together with small quantities of oxalic acid. The fumaric acid was identified, as before, by its physical properties, and by an analysis of its silver salt.

0.1508 grm. of the salt dried at 125° gave 0.1710 grm. AgBr.

	Calculated for $Ag_2C_4H_2O_4$.	Found.
Ag	65.46	65.15

The reaction with concentrated nitric acid is much more interesting, since the sulpho-group is in this way replaced by the nitro-group and the δ-nitropyromucic acid of Klinkhardt,* formed with comparatively little oxidation. This replacement is slowly effected at ordinary temperatures, but rapidly at 100°. Dry sulphopyromucic acid is slowly added to several times its weight of cold fuming nitric acid. The mixture is at first cooled, and the reaction afterward completed by gentle heat. The nitric acid is then partially removed by evaporation, and the nitropyromucic acid, which separates as the solution cools, recrystallized from hot water. For its complete purification we found it necessary to dissolve the acid in a cold dilute solution of sodic carbonate, to extract with ether this alkaline solution, and to recrystallize from hot water the product obtained by the addition of hydrochloric acid. The pale yellow acid thus obtained crystallized in rectangular plates, which melted at 182–183°.

0.4925 grm. substance gave 37.9 c.c. of moist nitrogen at 16° and under a pressure of 748 mm.

	Calculated for $C_5H_3(NO_2)O_3$.	Found.
N	8.91	8.82

The ethyl ether of the acid was easily formed by warming its alcoholic solution with concentrated sulphuric acid. It was sparingly soluble in cold alcohol, and crystallized in broad lustrous plates, which melted at 99–100°. Klinkhardt gives the melting-point of the acid as 183°, and of the ether as 101°.

With the δ-nitropyromucic acid is formed in small quantity a neutral substance containing nitrogen, which was obtained by evaporating the ether used in the extraction of the alkaline solution of the crude nitropyromucic acid. The same substance was formed in somewhat larger quantity when we attempted to prepare nitropyromucic acid without isolating the sulphonic acid by the addition of nitric acid to a solution of pyromucic acid in fuming sulphuric acid. The substance dissolved sparingly in boiling water, and crystallized on cooling in clustered prisms which melted at 100–101°. On warming with sodic hydrate a bright yellow color was developed. A filter paper moistened with its alcoholic solution and exposed to the vapors of ammonic sulphide turned yellow at first, then salmon-red. This behavior corresponds closely with that observed by V. Meyer* and Otto Stadler in the case of nitro derivatives of thiophen. Although from lack of material we have as yet made no analyses of this substance, we shall describe later a dibromdinitrofurfuran,† which was obtained under similar conditions from the $\beta\gamma$-dibrom-δ-sulphopyromucic acid, whose formation leaves no doubt that this substance is in fact aa-dinitrofurfuran. It will be further studied in the future in this Laboratory.

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* Journ. pr. Chemie N. F., xxv. 41.

Fusing potassic hydrate converts the δ-sulphopyromucic acid into succinic acid, and at the same time more or less oxalic acid is formed. Although we have also made certain experiments concerning the action of fusing sodic formiate, we have as yet reached no satisfactory conclusion, and must therefore postpone all consideration of our results until we have made further investigations.

β-BROM-δ-SULPHOPYROMUCIC ACID.

Although we have not succeeded in preparing substitution products directly from δ-sulphopyromucic acid, they may readily be made by the action of fuming sulphuric acid upon substituted pyromucic acids. If β-brompyromucic acid is dissolved in three times its weight of fuming sulphuric acid (Sp. Gr. 1.95), no carbonization takes place at ordinary temperatures, and from the diluted solution may be isolated by neutralization with baric carbonate the barium salt of β-brom-δ-sulphopyromucic acid. The free acid is extremely soluble even in cold water, and crystallizes in radiating needles which deliquesce rapidly in moist air.

Baric β-Brom-δ-Sulphopyromucate, $BaC_5HBrSO_6 \cdot 4\,H_2O$. — This salt is readily soluble in hot water, more sparingly soluble in cold water, and crystallizes in flat clustered prisms. It is precipitated in the form of fine needles on the addition of alcohol to its aqueous solution. The air-dried salt contains four molecules of water, most of which it loses over sulphuric acid, the rest at 100°.

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* Berichte d. deutsch. chem. Gesellsch., xvii. 2779.

† Page 205.

I. 1.9130 grm. of the air-dried salt lost, at 100°, 0.2824 grm. H_2O.
II. 1.1010 grm. of the air-dried salt lost, at 170°, 0.1630 grm. H_2O.

	Calculated for $BaC_5HBrSO_6 . 4 H_2O$.	Found. I.	II.
H_2O	15.06	14.76	14.80

I. 0.3030 grm. of the salt dried at 170° gave 0.1740 grm. $BaSO_4$.
II. 0.3293 grm. of the salt dried at 170° gave 0.1886 grm. $BaSO_4$.

	Calculated for BaC_5HBrSO_6.	Found. I.	II.
Ba	33.75	33.76	33.67

The solubility of the salt in cold water we determined according to the method of V. Meyer.

I. 27.6020 grm. of the solution saturated at 21° gave 0.2300 grm. $BaSO_4$.
II. 27.9011 grm. of the solution saturated at 21° gave 0.2369 grm. $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.
1.45	1.48

Calcic β-Brom-δ-Sulphopyromucate, $CaC_5HBrSO_6 . 6 H_2O$. — The calcium salt proved to be extremely soluble even in cold water. The syrupy solution gradually solidified with the separation of long radiating needles. The air-dried salt apparently contained six molecules of water, five of which it rapidly lost over sulphuric acid.

I. 1.2305 grm. of the air-dried salt lost, at 135°, 0.3193 grm. H_2O.
II. 0.4444 grm. of the air-dried salt gave 0.1413 grm. $CaSO_4$.

	Calculated for $CaC_5HBrSO_6 . 6 H_2O$.	Found. I.	II.
H_2O	25.90	25.95	
Ca	9.59		9.35

0.9631 grm. of the salt dried over sulphuric acid lost, at 135°, 0.0519 grm. H_2O.

	Calculated for $CaC_5HBrSO_6 . H_2O$.	Found.
H_2O	5.51	5.39

0.4608 grm. of the salt dried at 135° gave 0.1973 grm. $CaSO_4$.

	Calculated for CaC_5HBrSO_6.	Found.
Ca	12.94	12.60

Plumbic β-Brom-δ-Sulphopyromucate, $PbC_5HBrSO_6 . 4 H_2O$. — The lead salt is freely soluble in hot water, more sparingly in cold water, and crystallizes in flat clustered prisms, or on rapid cooling in clustered needles. The air-dried salt contains four molecules of water, almost the whole of which it rapidly loses over sulphuric acid.

I. 1.3814 grm. of the air-dried salt lost, at 130°, 0.1758 grm. H_2O.
II. 1.9209 grm. of the air-dried salt lost, at 140°, 0.2507 grm. H_2O.
III. 0.3442 grm. of the air-dried salt gave 0.1905 grm. $PbSO_4$.
IV. 0.6382 grm. of the air-dried salt gave 0.3530 grm. $PbSO_4$.

	Calculated for	Found.			
	$PbC_5HBrSO_6 . 4 H_2O$.	I.	II.	III.	IV.
H_2O	13.14	12.73	13.05		
Pb	37.78			37.80	37.79

Potassic β-Brom-δ-Sulphopyromucate, $K_2C_5HBrSO_6 . 1\frac{1}{2} H_2O$ (?). — This salt is readily soluble in cold water, more sparingly soluble in dilute alcohol. It crystallizes in small six-sided plates which are permanent in the air, but which effloresce over sulphuric acid. Two determinations of the water of crystallization made in different preparations agree precisely with each other, but do not correspond well with any simple formula for the salt.

I. 0.8184 grm. of the air-dried salt lost, at 160°, 0.0537 grm. H_2O.
II. 1.4398 grm. of the air-dried salt lost, at 160°, 0.0942 grm. H_2O.

	Calculated for	Calculated for	Found.	
	$K_2C_5HBrSO_6 . H_2O$.	$K_2C_5HBrSO_6 . 1\frac{1}{2} H_2O$.	I.	II.
H_2O	4.93	7.22	6.56	6.55

0.3652 grm. of the salt dried at 160° gave 0.1825 grm. K_2SO_4.

	Calculated for $K_2C_5HBrSO_6$.	Found.
K	22.52	22.44

The connection between this brom-sulphopyromucic acid and the δ-sulphopyromucic acid could evidently be proved most neatly and directly by eliminating from it the bromine, and examining carefully the sulphonic acid thus formed. By warming a strongly ammoniacal solution of the barium salt with zinc dust the bromine was quickly removed.

The filtered solution was boiled with a slight excess of baric hydrate until all the ammonia was expelled and the zinc precipitated. The solution was then freed from the excess of baric hydrate by means of carbonic dioxide, and concentrated on the water-bath. On cooling, the solution deposited globular aggregations of colorless crystals, which appeared to be identical with those of baric δ-sulphopyromucate. The identity was fully established by analyses of the salt, and by determinations of its solubility in water.

I. 1.5700 grm. of the air-dried salt lost, at 165°, 0.2803 grm. H_2O.
II. 0.7309 grm. of the air-dried salt gave 0.4295 grm. $BaSO_4$.

	Calculated for $BaC_5H_2SO_6 . 4 H_2O$.	Found. I.	Found. II.
H_2O	18.02	17.85	
Ba	34.34		34.55

0.4947 grm. of the salt dried at 165° gave 0.3505 grm. $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found.
Ba	41.90	41.67

I. 12.0595 grm. of the solution saturated at 21° gave 0.2985 grm. $BaSO_4$.
II. 12.1863 grm. of the solution saturated at 21° gave 0.2989 grm. $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.
3.47	3.44

These results are sufficient to prove that the sulphonic acid formed by the reduction of the β-brom-δ-sulphopyromucic acid is identical with that obtained directly from pyromucic acid by the action of sulphuric acid.

Action of Bromine.

Bromine in aqueous solution readily oxidizes β-brom-δ-sulphopyromucic acid or its salts. Since the relative position of the bromine and the sulpho-group had already been established, we thought it necessary to do no more than identify the final product of the oxidation. Bromine was added in slight excess to an aqueous solution of the barium salt, and the reaction completed at a gentle heat. The strongly acid solution was filtered from the baric sulphate which had been formed, and extracted with ether. The ether left on evaporation a white crystalline acid, which softened somewhat at 120° and melted completely at 165°. After two recrystallizations from water the acid melted sharply at 176–177°, and was therefore monobromfumaric acid. The oxidation took place according to the following equation: —

$$C_5H_3BrSO_6 + 3\,Br_2 + 4\,H_2O = C_4H_3BrO_4 + CO_2 + H_2SO_4 + 6\,HBr.$$

Action of Nitric Acid.

We have made no experiments concerning the action of dilute nitric acid upon β-brom-δ-sulphopyromucic acid, since it could safely be assumed that oxidation would ensue as with the δ-sulphopyromucic acid, and that monobromfumaric acid would be formed. It seemed to us, however, of decided interest to act upon the acid with fuming nitric acid, since a bromnitropyromucic acid should then result. Dry β-brom-δ-sulphopyromucic acid was slowly added to three times its weight of fuming nitric acid. The reaction progressed slowly in the cold, more rapidly on warming, and without any considerable oxidation. After the reaction was completed, the greater part of the nitric acid was expelled by gentle heat, the crystalline acid left was dissolved in a dilute solution of sodic carbonate, and the alkaline solution then extracted with ether. Upon evaporation of the ether a small quantity of a neutral oil was left, which gradually solidified. The quantity of the product which we thus obtained was so minute that further investigation was out of the question. The alkaline solution when acidified and again extracted with ether yielded in abundance a crystalline acid which proved to be β-brom-δ-nitropyromucic acid. It was readily soluble in alcohol, ether, or hot benzol, more sparingly in cold benzol. It dissolved freely in hot water, and as the solution cooled it was deposited in long clustered flattened needles, which contained one molecule of water. The anhydrous acid melted at 159–160°. At 100° the acid appeared to sublime slowly.

I. 1.2492 grm. of the acid crystallized from water lost, at 60°, 0.0911 grm. H_2O.*

II. 0.9980 grm. of the acid crystallized from water lost, at 78°, 0.0740 grm. H_2O.

	Calculated for $C_5H_2Br(NO_2)O_3 \cdot H_2O$.	Found.	
		I.	II.
H_2O	7.09	7.29	7.42

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* A slight mechanical loss renders the result of this determination uncertain in the second decimal place.

I. 0.2065 grm. of the acid dried at 100° gave 0.1652 grm. AgBr.

II. 0.2648 grm. of the acid dried at 100° gave 14.2 c.c. of moist nitrogen at 20° and under a pressure of 763 mm.

	Calculated for $C_5H_2Br(NO_2)O_3$.	Found. I.	II.
Br	33.90	34.04	
N	5.93		6.15

This acid will be further studied in this Laboratory. There can be no doubt, however, that, like the nitropyromucic acid of Klinkhardt, it contains the nitro-group in the δ position.

βγ-DIBROM-δ-SULPHOPYROMUCIC ACID.

βγ-dibrompyromucic acid dissolves in fuming sulphuric acid without the slightest carbonization, and is converted in a short time into the corresponding sulphonic acid. A large part of our work was done with material made from pure βγ-dibrompyromucic acid. We subsequently found, however, as will be described more at length later in this paper, that the βδ-dibrompyromucic was but little affected by fuming sulphuric acid if the action were not too long continued, and that the mixture of the isomeric dibrompyromucic acids obtained from pyromucic tetrabromide could therefore advantageously be employed direct. The mixed acids were dissolved in once and a half their weight of fuming sulphuric acid, and the solution diluted with water after the lapse of two or three hours. The βδ-dibrompyromucic acid thus precipitated was removed by filtration, and the solution neutralized as usual by baric carbonate. The small amount of βδ-dibrompyromucic acid, or its decomposition products, which remained in solution, could readily be removed by the recrystallization of the barium salt which was obtained after evaporation. Since the separation of the isomeric dibrompyromucic acids is a matter of some difficulty, the preparation of the sulphonic acid in question is thus greatly facilitated. The free acid is very soluble even in cold water, but is more sparingly soluble in ordinary concentrated sulphuric acid. From sulphuric acid it crystallizes in clustered needles, from water it is deposited in broad flat prisms, which are permanent under ordinary atmospheric conditions.

Baric βγ-Dibrom-δ-Sulphopyromucate, $BaC_5Br_2SO_6 . 5 H_2O$. — This salt is very readily soluble in hot water, more sparingly in cold water. The hot saturated solution solidifies on cooling, with the separation of long silky radiating needles. The air-dried salt contains five molecules of water, a part of which it loses over sulphuric acid.

I. 1.5136 grm. of the air-dried salt lost, at 125°, 0.2422 grm. H_2O.
II. 1.7684 grm. of the air-dried salt lost, at 160°, 0.2855 grm. H_2O.
III. 2.5118 grm. of the air-dried salt lost, at 180°, 0.4013 grm. H_2O.

	Calculated for $BaC_5Br_2SO_6 . 5 H_2O$.	Found.		
		I.	II.	III.
H_2O	15 65	16.01	16.14	15.97

I. 0.5378 grm. of the salt dried at 125° gave 0.2575 grm. $BaSO_4$.
II. 0.4688 grm. of the salt dried at 180° gave 0.2243 grm. $BaSO_4$.
III. 0.5317 grm. of the salt dried at 180° gave 0.2550 grm. $BaSO_4$.

	Calculated for $BaC_5Br_2SO_6$	Found.		
		I.	II.	III.
Ba	28.25	28.15	28.13	28.19

The solubility of the salt in cold water we determined in the usual way.

I. 10.9011 grm. of the solution saturated at 20° gave 0.2170 grm. $BaSO_4$.
II. 11.9609 grm. of the solution saturated at 20° gave 0.2398 grm. $BaSO_4$.

The solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.
4.14	4.17

When an aqueous solution of the barium salt is evaporated at 100°, small clear prisms separate, which contain less water than the salt just described. We found it impossible to prepare this salt satisfactorily for analysis, since it at once took up water in the cold. A preparation which was removed from the hot solution and immediately dried by pressure with filter paper gave on analysis the following results: —

I. 1.6161 grm. of the salt lost, at 140°, 0.1767 grm. H_2O.
II. 0.6265 grm. of the salt gave 0.2665 grm. $BaSO_4$.

	Calculated for $BaC_5Br_2SO_6 . 3 H_2O$.	Found.	
		I.	II.
H_2O	10.02	10.93	
Ba	25.42		25.01

Plumbic βγ-Dibrom-δ-Sulphopyromucate, $PbC_5Br_2SO_6 . 4 H_2O$. — The lead salt is readily soluble in hot water, more sparingly in cold, and crystallizes in fine felted needles, which are permanent in the air, but effloresce over sulphuric acid.

I. 1.4993 grm. of the air-dried salt lost, at 165°, 0.1686 grm. H_2O.
II. 1.0386 grm. of the air-dried salt lost, at 165°, 0.1159 grm. H_2O.
III. 0.6246 grm. of the air-dried salt gave 0.3015 grm. $PbSO_4$.

	Calculated for $PbC_5Br_2SO_6 . 4 H_2O$.	Found. I.	II.	III.
H_2O	11.48	11.24	11.16	
Pb	33.01			32.98

0.5019 grm. of the salt dried at 165° gave 0.2741 grm. $PbSO_4$.

	Calculated for $PbC_5Br_2SO_6$.	Found.
Pb	37.32	37.32

Argentic βγ-Dibrom-δ-Sulphopyromucate, $Ag_2C_5Br_2SO_6 . H_2O$. — The silver salt is sparingly soluble in cold water, more readily in hot, and crystallizes in large rhombic plates.

1.0216 grm. of the air-dried salt lost, at 120°, 0.0339 grm. H_2O.

	Calculated for $Ag_2C_5Br_2SO_6 . H_2O$.	Found.
H_2O	3.09	3.31

I. 0.3016 grm. of the salt dried at 120° gave 0.1520 grm. AgCl.
II. 0.3021 grm. of the salt dried at 120° gave 0.1522 grm. AgCl.

	Calculated for $Ag_2C_5Br_2SO_6$.	Found. I.	II.
Ag	38.30	37.93	37.93

Potassic βγ-Dibrom-δ-Sulphopyromucate, $K_2C_5Br_2SO_6 . H_2O$. — The potassium salt is readily soluble in hot water, more sparingly soluble in cold water. It crystallizes in flat obliquely truncated prisms.

I. 1.0634 grm. of the air-dried salt lost, at 135°, 0.0377 grm. H_2O.
II. 0.5307 grm. of the air-dried salt gave 0.2072 grm. K_2SO

	Calculated for $K_2C_5Br_2SO_6 . H_2O$.	Found. I.	II.
H_2O	4.05	3.55	
K	17.60		17.53

0.4507 grm. of the salt dried at 135° gave 0.1823 grm. K_2SO_4.

	Calculated for $K_2C_5Br_2SO_6$.	Found.
K	18.35	18.16

From the structure of the βγ-dibrompyromucic acid, which has already been determined by Hill and Sanger,* it is evident that a sulphonic acid formed from it must of necessity contain the sulpho-group in the δ position. It therefore seemed to us of interest to prepare from this βγ-dibrom-δ-sulphopyromucic acid, by the elimination of the bromine, the corresponding sulphopyromucic acid. Should this acid prove to be identical with that made directly from pyromucic acid by means of sulphuric acid, the δ position of the sulpho-group in the latter acid would be established with precision. A strongly ammoniacal solution of baric βγ-dibrom-δ-sulphopyromucate was warmed for some time with an excess of zinc-dust. After reduction had taken place the filtered solution was boiled with an excess of baric hydrate until the ammonia had been expelled, and the excess of baric hydrate then removed with carbonic dioxide. The concentrated solution deposited on cooling hemispherical aggregations of colorless crystals, which upon investigation proved to be identical in composition with the baric sulphopyromucate already described, and to have also the same solubility in cold water.

0.6194 grm. of the air-dried salt lost, at 160°, 0.1111 grm. H_2O, and gave 0.3614 grm. $BaSO_4$.

	Calculated for $BaC_5H_2SO_6 . 4 H_2O$.	Found.
H_2O	18.02	17.94
Ba	34.34	34.30

I. 12.9988 grm. of the solution saturated at 21° gave 0.3169 grm. $BaSO_4$.
II. 13.0993 grm. of the solution saturated at 21° gave 0.3181 grm. $BaSO_4$.

The aqueous solution saturated at 21°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.
3.42	3.41

It will be seen that these results prove the identity of this salt with that made directly from pyromucic acid.

Action of Bromine.

Bromine in aqueous solution readily oxidizes βγ-dibrom-δ-sulphopyromucic acid or its salts. If a slight excess of bromine is added to an aqueous solution of the barium salt, baric sulphate is at once precipitated, and after the reaction is completed by gentle heat ether extracts from the filtered solution dibrommaleic acid. The anhydride formed by sublimation was found to melt at the proper point, 114–115°.

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* These Proceedings, xxi. 181.

Action of Nitric Acid.

Diluted nitric acid oxidizes $\beta\gamma$-dibrom-δ-sulphopyromucic acid on heating and forms dibrommaleic acid, whose identity we established through the melting-point of its anhydride, 114–115°. By the action of fuming nitric acid a nitro-acid is formed. The dry acid was slowly added to several times its weight of fuming nitric acid. At first the mixture was cooled, afterwards warmed and the greater part of the nitric acid then expelled by gentle heat. The crystalline product of the reaction was in part an acid quite readily soluble in hot water, and in part a neutral substance which dissolved with more difficulty in boiling water. For the complete separation of these two substances we treated the product with a dilute solution of sodic carbonate and extracted with ether. The alkaline solution was then acidified and the acid extracted with ether. After several recrystallizations from hot water, it formed finely felted yellow needles, which were sparingly soluble in cold water, more readily in hot, and melted at 204–205°. They dissolved freely in alcohol, ether, or in benzol. Analysis showed the substance to be a dibromnitropyromucic acid.

I. 0.1050 grm. of the acid gave 0.1260 grm. AgBr.
II. 0.2970 grm. of the acid gave 11.7 c. c. of moist nitrogen at 21° under a pressure of 758 mm.

	Calculated for $C_5HBr_2(NO_2)O_3$.	Found.
Br	50.79	51.07
N	4.44	4.47

The mode of its formation shows that this acid must of necessity be the $\beta\gamma$-dibrom-δ-nitropyromucic acid.

The ether which had been used for extracting the alkaline solution of the crude nitro product left, on evaporation, a quantity of a yellow crystalline solid, which was sufficient to enable us to establish its identity by analysis. The substance was sparingly soluble even in hot water, and crystallized on slow cooling in stout prisms, or on rapid cooling and scratching in felted needles. In alcohol it was sparingly soluble; but benzol dissolved it freely, and on standing the solution deposited quite large transparent yellow prisms, which effloresced rapidly on exposure to the air. The melting point to the effloresced substance was 150–151°, and the percentage of bromine it contained showed that it was a dibromdinitrofurfuran.

0.2008 grm. of the substance gave 0.2396 grm. AgBr.

	Calculated for $C_4Br_2(NO_2)_2O$.	Found.
Br	50.63	50.79

The clear crystals deposited from benzol evidently contained benzol of crystallization. They effloresced so rapidly, however, that the exact determination of the combined benzol was somewhat difficult.

0.2611 grm. of the substance rapidly pressed and weighed lost, on standing exposed to the air until the weight was constant, 0.0486 grm. benzol.

	Calculated for $C_4Br_2(NO_2)_2O \cdot C_6H_6$.	Found.
C_6H_6	19.80	18.61

Considering the difficulty of such determinations, this result leaves no doubt that this dibromdinitrofurfuran crystallizes with one molecule of benzol. The mode of formation of this substance leaves no possible doubt that it is the *αα*-dinitro-*ββ*-dibromfurfuran.

β-Sulpho-δ-Brompyromucic Acid.

The three sulphonic acids thus far described contain the sulpho-group in the δ position, and, in the two cases where the formation of isomeric products is theoretically possible, we have hitherto been unable to prove that any isomeric sulphonic acids are in reality formed. For the preparation of such isomeric products it was, therefore, evidently necessary to start with the δ-hydrogen atom otherwise replaced, and the δ-brompyromucic acid formed the most convenient material. We found no difficulty in preparing in this way a sulphonic acid, which we have called the β-sulpho-δ-brompyromucic acid, and from it the β-sulphopyromucic acid itself may be made. Since the brominated acid was of necessity first prepared, and we were able to investigate it more fully, it may be more conveniently first described.

δ-brompyromucic acid dissolves in fuming sulphuric acid without essential decomposition, and after the lapse of some time the formation of the sulphonic acid appears to be complete. On neutralizing the diluted solution with baric carbonate, a barium salt is obtained which is sparingly soluble even in hot water, and which usually persistently retains a slight yellow or greenish color. The purification of this neutral salt is still further rendered difficult by the fact that a hot saturated solution of the salt deposits little or nothing on cooling, and recrystallization therefore involves the evaporation of comparatively large quantities of liquid. The purification may be more conveniently effected by conversion into the more soluble acid salt, or by preparing the acid salt at the outset. The acid salt may easily be made by dissolving the neutral salt in hydrochloric acid somewhat diluted with water, and removing by recrystallization the baric chloride formed. From a solution of the acid salt the neutral salt may again be precipitated by the addition of baric acetate, or of course by the addition of ammonic hydrate and the necessary quantity of baric chloride. The free acid made from the barium salt by exact precipitation with sulphuric acid forms oblique flat prisms or plates, which deliquesce in moist air.

Baric β-Sulpho-δ-brompyromucate, $BaC_5HBrSO_6 \cdot 5 H_2O$. — The barium salt is sparingly soluble in hot or cold water, and crystallizes in clear six-sided, clustered prisms. Its aqueous solution is precipitated by the addition of alcohol. The salt contains five molecules of water, four of which it loses slowly on exposure to the air, or more rapidly when heated to 100°.

I. 2.1588 grm. of the salt dried by short exposure to the air lost, at 162°, 0.3806 grm. H_2O.
II. 1.1795 grm. of the salt dried by short exposure to the air lost, at 170°, 0.2010 grm. H_2O.

	Calculated for $BaC_5HBrSO_6 \cdot 5 H_2O$.	Found.	
		I.	II.
H_2O	18.14	17.63	17.88

I. 1.8574 grm. of the salt dried at 100° lost, at 162°, 0.0792 grm. H_2O.
II. 0.7262 grm. of the salt dried at 100° lost, at 160°, 0.0317 grm. H_2O.

	Calculated for $BaC_5HBrSO_6 \cdot H_2O$.	Found.	
		I.	II.
H_2O	4.25	4.28	4.37

I. 0.6945 grm. of the salt dried at 160° gave 0.3980 grm. $BaSO_4$.
II. 0.7840 grm. of the salt dried at 140° gave 0.4500 grm. $BaSO_4$.
III. 0.7825 grm. of the salt dried at 140° gave 0.4495 grm. $BaSO_4$.

	Calculated for BaC_5HBrSO_6.	Found.		
		I.	II.	III.
Ba	33.75	33.69	33.75	33.77

We also determined the solubility of the salt in water at ordinary temperatures. Since the hot saturated solution deposited little or nothing on cooling, we prepared the solution by boiling down the hot aqueous solution until the salt began to separate. On cooling this supersaturated solution, abundant crystals were deposited.

I. 32.6032 grm. of the solution saturated at 20° gave 0.5016 grm. $BaSO_4$.
II. 33.7864 grm. of the solution saturated at 20° gave 0.5194 grm. $BaSO_4$.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.
2.68	2.68

Acid Baric β-Sulpho-δ-brompyromucate, $Ba(C_5H_2BrSO_6)_2 . 4 H_2O$. — This salt is most easily prepared by dissolving the neutral barium salt in diluted hydrochloric acid. It is readily soluble in hot water, sparingly in cold water, and crystallizes in large well-formed prisms, which appear to be triclinic. The salt loses nothing when exposed to the air, or over sulphuric acid, and the loss at 100° is also insignificant. At 130° it slowly loses in weight, but turns brown and suffers partial decomposition before complete dehydration is reached.

I. 0.7884 grm. of the air-dried salt gave 0.2456 grm. $BaSO_4$.
II. 0.7804 grm. of the air-dried salt gave 0.2460 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_2BrSO_6)_2 . 4 H_2O$.	Found.	
		I.	II.
Ba	18.29	18.32	18.53

Calcic β-Sulpho-δ brompyromucate, $CaC_5HBrSO_6 . 2 H_2O$. — The calcium salt is quite readily soluble in cold water, and its solubility is but little increased by heat. It crystallizes in compactly aggregated oblique prisms, which are permanent in the air, and lose but little in weight over sulphuric acid or when heated to 100°.

I. 1.7804 grm. of the air-dried salt lost, at 205°, 0.1767 grm. H_2O.
II. 0.6483 grm. of the air-dried salt gave 0.2544 grm. $CaSO_4$.

	Calculated for $CaC_5HBrSO_6 . 2 H_2O$.	Found.	
		I.	II.
H_2O	10.42	9.92	
Ca	11.60		11.54

I. 0.4645 grm. of the salt dried at 200° gave 0.2015 grm. $CaSO_4$.
II. 0.4026 grm. of the salt dried at 200° gave 0.1758 grm. $CaSO_4$.

	Calculated for CaC_5HBrSO_6.	Found. I.	Found. II.
Ca	12.94	12.76	12.83

Plumbic β-Sulpho-δ-brompyromucate, PbC_5HBrSO_6. — The lead salt is tolerably soluble in cold water, and its solubility is but little increased by heat. The salt dried by exposure to the air contains one and a half molecules of water, one molecule of which it retains when dried over sulphuric acid.

I. 1.5047 grm. of the air-dried salt lost, at 150°, 0.0815 grm. H_2O, and gave 0.9074 grm. $PbSO_4$.
II. 1.7254 grm. of the air-dried salt lost, at 150°, 0.0925 grm. H_2O.
III. 0.5361 grm. of the air-dried salt gave 0.3239 grm. $PbSO_4$.

	Calculated for $PbC_5HBrSO_6 . 1\frac{1}{2} H_2O$.	Found. I.	Found. II.	Found. III.
H_2O	5.37	5.42	5.36	
Pb	41.15	41.20		41.27

1.6958 grm. of the salt dried over sulphuric acid lost, at 150°, 0.0629 grm. H_2O.

	Calculated for $PbC_5HBrSO_6 . H_2O$.	Found.
H_2O	3.64	3.71

I. 0.5894 grm. of the salt dried at 150° gave 0.3743 grm. $PbSO_4$.
II. 0.6496 grm. of the salt dried at 150° gave 0.4122 grm. $PbSO_4$.

	Calculated for PbC_5HBrSO_6.	Found. I.	Found. II.
Pb	43.49	43.38	43.35

Argentic β-Sulpho-δ-brompyromucate, $Ag_2C_5HBrSO_6 . 2 H_2O$. — The silver salt is sparingly soluble in cold water, and crystallizes in plates which contain two molecules of water.

1.3888 grm. of the air-dried salt lost, at 115°, 0.0968 grm. H_2O.

	Calculated for $Ag_2C_5HBrSO_6 . 2 H_2O$.	Found.
H_2O	6.91	6.97

I. 0.1715 grm. of the salt dried at 115° gave, on precipitation with HBr, 0.1340 grm. AgBr.
II. 0.1725 grm. of the salt dried at 115° gave, on precipitation with HBr, 0.1337 grm. AgBr.

III. 0.4347 grm. of the salt dried at 115° gave, on heating with HNO_3, 0.1684 grm. AgBr and 0.2082 grm. $BaSO_4$.

IV. 0.5100 grm. of the salt dried at 115° gave, on heating with HNO_3, 0.1980 grm. AgBr.

	Calculated for $Ag_2C_5HBrSO_6$.	Found. I.	II.	III.	IV.
Ag	44.54	44.88	44.53		
SO_3	16.50			16.44	
Br	16.50			16.49	16.52

Potassic β-Sulpho-δ-brompyromucate, $K_2C_5HBrSO_6$. — The potassium salt is very soluble in cold water, and crystallizes in thick rhombic plates which are anhydrous.

I. 0.4510 grm. of the salt gave 0.2247 grm. K_2SO_4.
II. 0.5020 grm. of the salt gave 0.2530 grm. K_2SO_4.

	Calculated for $K_2C_5HBrSO_6$.	Found. I.	II.
K	22.52	22.37	22.62

Action of Bromine.

Bromine in aqueous solution acts with readiness upon β-sulpho-δ-brompyromucic acid or its salts. The products vary with the conditions chosen. If one molecule of bromine is slowly added to a cold aqueous solution of the barium salt, carbonic dioxide is evolved and baric dibromfurfuran sulphonate is formed together with baric bromide. This reaction is obviously identical with that noticed by Hill and Hartshorn[*] in the decomposition of δ-brompyromucic acid in alkaline solution by bromine in which *aa*-dibromfurfuran is formed. If the baric β-sulpho-δ-brompyromucate is suspended in a little water, and bromine slowly added, the salt at first dissolves and soon after the baric dibromfurfuran sulphonate crystallizes out. From a more dilute solution the salt can readily be obtained by evaporation. In the latter case, the solution is but feebly acid and the yield nearly quantitative.

Baric aa-Dibromfurfuran-β-sulphonate, $Ba(C_4HBr_2SO_4)_2 \cdot H_2O$. — This salt is quite readily soluble in hot water, more sparingly in cold water, and crystallizes in pearly scales or plates.

I. 0.8179 grm. of the air-dried salt lost, at 135°, 0.0204 grm. H_2O.
II. 0.8833 grm. of the air-dried salt lost, at 125°, 0.0224 grm. H_2O.

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[*] Berichte d. deutsch. chem. Gesellsch., xviii. 448.

	Calculated for $Ba(C_4HBr_2SO_4)_2 . H_2O$.	Found. I.	II.
H_2O	2.35	2.49	2.54

I. 0.3952 grm. of the salt dried at 135° gave 0.1238 grm. $BaSO_4$.
II. 0.3932 grm. of the salt dried at 135° gave 0.1223 grm. $BaSO_4$.
III. 0.4219 grm. of the salt dried at 125° gave 0.1320 grm. $BaSO_4$.

	Calculated for $Ba(C_4HBr_2SO_4)_2$.	Found. I.	II.	III.
Ba	18.40	18.42	18.28	18.40

Potassic αα-Dibromfurfuran-β-sulphonate, $KC_4HBr_2SO_4$. — The potassium salt can readily be made by the action of bromine upon a slightly alkaline solution of potassic β-sulpho-δ-brompyromucate. It crystallizes in well-formed prisms which are anhydrous.

I. 0.3725 grm. of the salt gave 0.4090 grm. AgBr, and 0.2540 grm. $BaSO_4$.
II. 0.3329 grm. of the salt gave 0.3649 grm. AgBr, and 0.2283 grm. $BaSO_4$.

	Calculated for $KC_4HBr_2SO_4$.	Found. I.	II.
Br	46.49	46.73	46.66
SO_3	23.25	23.41	23.55

Bromine in aqueous solution readily attacks the salts of the *αα*-dibromfurfuran-β-sulphonic acid; so that, if an excess of bromine is added to a salt of β-sulpho-δ-brompyromucic acid, only the products of this second stage of the reaction are obtained. The oxidation goes on slowly at ordinary temperatures, more rapidly on warming, and even after treating for a long time at 100° with an excess of bromine no appreciable amount of sulphuric acid is formed. The final product of the reaction is an acid containing the sulpho-group, which we have named, provisionally at least, sulphofumaric acid. The acid itself we found to be extremely soluble in water, and upon evaporating the aqueous solution *in vacuo* a viscous residue was obtained which did not crystallize even after long standing. The barium, lead, and silver salts of the acid were very sparingly soluble even in boiling water. The calcium and potassium salts, on the other hand, were very soluble even in cold water, and could not be obtained in crystalline form. As might have been expected, the strontium salt proved to be more readily soluble than the barium salt, but it did not crystallize well from water. We also found it impossible to prepare an acid salt the properties of which were more favorable to purification. We therefore prepared and analyzed the barium and silver salts.

Baric Sulphofumarate, $Ba_3(C_4HSO_7)_2 \cdot x\, H_2O$. — To an aqueous solution of baric β-sulpho-δ-brompyromucate we added a slight excess of bromine, and finished the reaction by the aid of heat. The strongly acid solution thus obtained was partially neutralized by the addition of baric carbonate, the carbonic dioxide expelled by long boiling, and baric hydrate then added to alkaline reaction. In this way a voluminous flocculent precipitate was thrown down, which was dissolved in boiling dilute hydrochloric acid and reprecipitated by ammonic hydrate. Although the baric sulphofumarate was markedly soluble in a solution of ammonic chloride, the analytical results were more satisfactory than when the salt was again precipitated by baric hydrate. The voluminous precipitate, when thoroughly washed and dried by exposure to the air, formed a light, porous hygroscopic mass, which gave us on analysis varying percentages. The salt dried at 130° gave, however, a constant percentage of barium corresponding to that required by a salt with three molecules of water, and even at 200° one molecule of water appeared to be retained. In each case, however, the ratio between the barium and sulphur was found to be as 3 to 2.

0.6486 grm. of the air-dried salt gave, after fusion with Na_2CO_3 and $KClO_3$, 0.4918 grm. $BaSO_4$(Ba) and 0.3310 grm. $BaSO_4(SO_3)$.

	Calculated for $Ba_3(C_4HSO_7)_2 \cdot 7\, H_2O$.	Found.
Ba	44.52	44.58
SO_3	17.34	17.52

$Ba : SO_3 = 2.97 : 2.$

Here it will be seen that the air-dried salt contained seven molecules of water. This, however, must have been an accidental coincidence, since the same salt after several days further exposure to the air, contained more water.

1.2865 grm. of the air-dried salt lost, at 200°, 0.1686 grm. H_2O.

	Calculated for $Ba_3(C_4HSO_7)_2 \cdot 7\, H_2O$.	Found.
$6\, H_2O$	11.70	13.10

0.5471 grm. of the salt dried at 200° gave 0.4706 grm. $BaSO_4$(Ba), and 0.3159 grm. $BaSO_4(SO_3)$.

	Calculated for $Ba_3(C_4HSO_7)_2 \cdot H_2O$.	Found.
Ba	50.42	50.56
SO_3	19.63	19.82

$Ba : SO_3 = 2.98 : 2.$

I. 1.1659 grm. of the salt dried at 130° lost, at 200°, 0.0480 grm. H_2O.
II. 0.4608 grm. of the salt dried at 130° gave 0.3798 grm. $BaSO_4$.
III. 0.5175 grm. of the salt dried at 130° gave 0.4256 grm. $BaSO_4$.

	Calculated for $Ba_3(C_4HSO_7)_2 . 3 H_2O$.	Found. I.	II.	III.
$2 H_2O$	4.23	4.12		
Ba	48.29		48.45	48.35

In the sulphuric acid determinations given above, the baric sulphate was precipitated in the presence of large quantities of sodium and potassium salts. Although it was purified in the usual way before weighing, the results are undoubtedly still somewhat too high.

Argentic Sulphofumarate, $Ag_3C_4HSO_7 . x H_2O$. — On adding a solution of ammonic sulphofumarate to an excess of argentic nitrate, the silver salt is thrown down as a heavy curdy precipitate, which frequently becomes crystalline on standing. It is very sparingly soluble in cold water, somewhat more readily in hot. The air-dried salt contains water, a part of which at least it loses at 100°. At 110° it loses more rapidly in weight, but decomposition ensues at the same time. A sample of the salt which had been dried for some time at 100°, but which was still losing very slowly in weight, was analyzed with the following results: —

I. 0.4448 grm. of the salt gave 0.4673 grm. AgBr, and 0.1933 grm. $BaSO_4$.
II. 0.4834 grm. of the salt gave 0.2933 grm. Ag.

	Calculated for $Ag_3C_4HSO_7 . H_2O$.	Found. I.	II.
Ag	60.54	60.39	60.67
SO_3	14.95	14.92	

$$Ag : SO_3 = 3.01 : 1.$$

The air-dried salt had already lost at 100° about one molecule of water.

1.0317 grm. of the air-dried salt lost, at 100°, 0.0368 grm. H_2O.

	Calculated for $Ag_3C_4HSO_7 . 2 H_2O$.	Found.
$1 H_2O$	3.26	3.57

The air-dried salt, therefore, appeared to contain two molecules of water. The analysis of a second preparation of the air-dried salt gave substantially the same ratio between silver and sulphur, and yet showed that the salt contained a lower percentage of silver.

0.4680 grm. of the air-dried salt gave 0.3561 grm. AgCl and 0.2009 grm. $BaSO_4$.

	Calculated for $Ag_3C_4HSO_7 \cdot 2\,H_2O$.	Found.
Ag	58.59	57.28
SO_3	14.46	14.73

$Ag : SO_3 = 2.88 : 1.$

By drying over sulphuric acid the precipitated silver salt, we were unable to obtain it with any more definite or constant percentages of water.

The lead salt is almost insoluble in water or in dilute acetic acid; but we have been unable as yet to obtain any results on analysis which were wholly satisfactory.

There can be no doubt that β-sulpho-δ-brompyromucic acid is decomposed by bromine in aqueous solution according to the following equations:—

$$C_5H_3BrSO_6 + Br_2 = C_4H_2Br_2SO_4 + CO_2 + HBr.$$
$$C_4H_2Br_2SO_4 + Br_2 + 3\,H_2O = C_4H_4SO_7 + 4\,HBr.$$

Action of Nitric Acid.

The decomposition of β-sulpho-δ-brompyromucic acid with nitric acid we have followed qualitatively. We have been unable hitherto to effect a replacement of the sulpho-group by the action of fuming nitric acid, as we had so readily done with the δ-sulphonic acids. In this case, whatever was the strength of the nitric acid, we could only prove the formation of an acid which was identical in its behavior with sulphofumaric acid. Not unfrequently, however, the oxidation had gone further, and oxalic acid was also formed together with sulphuric acid.

We have made a few experiments concerning the action of fusing potassic hydrate upon potassic β-sulpho-δ-brompyromucate, and have as yet been able to prove the formation of nothing but oxalic acid. While it is doubtful whether any other product but oxalic acid is normally formed, we shall study the reaction further, as well as the action of fusing sodic formiate.

β-SULPHOPYROMUCIC ACID.

The ammoniacal solution β-sulpho-δ-brompyromucic acid is reduced without difficulty by zinc dust. A strongly ammoniacal solution of the barium salt was heated for some time with an excess of zinc dust, the filtered solution boiled with the addition of baric hydrate till ammonia was no longer given off, and the excess of baric hydrate precipitated with carbonic dioxide. The solution thus obtained yielded on evaporation the barium salt of β-sulphopyromucic acid in satisfactory quantity. Since this salt was very nearly if not quite as soluble in cold water as in hot, its purification could most conveniently be effected by conversion into the acid salt, which was readily soluble in hot water, but sparingly in cold water.

Baric β-Sulphopyromucate, $BaC_5H_2SO_6 . 3 H_2O$. — This salt is sparingly soluble in hot water, and the hot saturated solution deposits nothing on cooling. By evaporation *in vacuo* over sulphuric acid, the salt is obtained in clean obliquely terminated plates, which contain three molecules of water.

I. 1.5356 grm. of the air-dried salt lost, at 160°, 0.2156 grm. H_2O.
II. 1.2179 grm. of the air-dried salt lost, at 160°, 0.1707 grm. H_2O.
III. 0.7448 grm. of the air-dried salt gave 0.4571 grm. $BaSO_4$.

	Calculated for $BaC_5H_2SO_6 . 3 H_2O$.	Found.		
		I.	II.	III.
H_2O	14.18	14.05	14.02	
Ba	35.96			36.08

I. 0.7139 grm. of the salt dried at 160° gave 0.5092 grm. $BaSO_4$.
II. 0.7303 grm. of the salt dried at 160° gave 0.5197 grm. $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found.	
		I.	II.
Ba	41.90	41.94	41.84

If the solution is evaporated at 100°, the salt separates in small clear prisms with oblique truncations, which appear to contain one molecule of water.* If the salt is removed while the solution is hot, it contains a somewhat lower percentage of water (IV.) than it does when the solution is first allowed to cool (I., II., and III.). In the latter case it undoubtedly contains a slight admixture of the salt containing three molecules of water.

I. 4.2755 grm. of the air-dried salt lost, at 165°, 0.2510 grm. H_2O.
II. 2.1345 grm. of the air-dried salt lost, at 165°, 0.1290 grm. H_2O.

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* In a preliminary paper (Berichte d. deutsch. chem. Gesellsch., xviii. 2095) the baric β-sulphopyromucate was described as containing but one molecule of water. At that time the salt obtained by evaporation at 100° had alone been analyzed.

III. 0.5901 grm. of the air-dried salt gave 0.3981 grm. $BaSO_4$.
IV. 0.8840 grm. of the air-dried salt lost, at 160°, 0.0484 grm. H_2O.

	Calculated for	Found.			
	$BaC_5H_2SO_6 . H_2O$.	I.	II.	III.	IV.
H_2O	5.22	5.87	6.04		5.47
Ba	39.71			39.66	

I. 0.6005 grm. of the salt dried at 165° gave 0.4270 grm. $BaSO_4$.
II. 0.6010 grm. of the salt dried at 165° gave 0.4269 grm. $BaSO_4$.

	Calculated for	Found.	
	$BaC_5H_2SO_6$.	I.	II.
Ba	41.90	41.79	41.76

In determining the solubility of the barium salt in cold water, we evaporated its solution rapidly until crystals began to appear, and then cooled with constant stirring. Abundant crystals of the salt were thus formed. In order to satisfy ourselves that solutions of constant composition could be obtained in this way, we made four separate determinations.

I. 16.2601 grm. of the solution saturated at 21° gave 0.2172 grm. $BaSO_4$.
II. 14.4321 grm. of the solution saturated at 21° gave 0.1950 grm. $BaSO_4$.
III. 12.1256 grm. of the solution saturated at 21° gave 0.1646 grm. $BaSO_4$.
IV. 12.7701 grm. of the solution saturated at 21° gave 0.1788 grm. $BaSO_4$.

The aqueous solution of barium salt saturated at 21°, therefore, contained the following percentages of the anhydrous salt: —

I.	II.	III.	IV.
1.88	1.90	1.91	1.96

Acid Baric β-Sulphopyromucate, $Ba(C_5H_3SO_6)_2 . 3 H_2O$. — This salt may be made by dissolving the neutral barium salt in hydrochloric acid, or, more advantageously, by mixing solutions of the neutral barium salt and the free acid in equivalent quantities. It is readily soluble in hot water, more sparingly in cold water, and crystallizes in small obliquely truncated prisms, which are permanent in the air.

I. 1.4255 grm. of the air-dried salt lost, at 130°, 0.1403 grm. H_2O.
II. 1.3386 grm. of the air-dried salt lost, at 135°, 0.1271 grm. H_2O.
III. 0.5371 grm. of the air-dried salt gave 0.2193 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2 . 3 H_2O$.	Found. I.	 II.	 III.
H_2O	9.42	9.84	9.49	
Ba	23.91			24.00

I. 0.3068 grm. of the anhydrous salt gave 0.1378 grm. $BaSO_4$.
II. 0.3128 grm. of the anhydrous salt gave 0.1409 grm. $BaSO_4$.

	Calculated for $Ba(C_5H_3SO_6)_2$.	Found. I.	 II.
Ba	26.39	26.41	26.48

Calcic β-Sulphopyromucate, $CaC_5H_2SO_6 . 2 H_2O$. — The calcium salt is quite readily soluble in cold water, and separates on evaporation in crusts. By the addition of alcohol to a cold aqueous solution the salt is precipitated in the form of small prisms, which, when dried by exposure to the air, contain two molecules of water.

I. 1.0454 grm. of the air-dried salt lost, at 130°, 0.1444 grm. H_2O.
II. 1.0285 grm. of the air-dried salt lost, at 135°, 0.1415 grm. H_2O.

	Calculated for $CaC_5H_2SO_6 . 2 H_2O$.	Found. I.	 II.
H_2O	13.53	13.81	13.74

I. 0.4790 grm. of the anhydrous salt gave 0.2825 grm. $CaSO_4$.
II. 0.4118 grm. of the anhydrous salt gave 0.2425 grm. $CaSO_4$.

	Calculated for $CaC_5H_2SO_6$.	Found. I.	 II.
Ca	17.40	17.35	17.32

Potassic β-Sulphopyromucate, $K_2C_5H_2SO_6 . 2\frac{1}{2} H_2O$. — The potassium salt is extremely soluble in water, and crystallizes in long prisms. It separates in the form of fine needles on the addition of alcohol to its aqueous solution.

1.2358 grm. of the air-dried salt lost, at 140°, 0.1788 grm. H_2O.

	Calculated for $K_2C_5H_2SO_6 . 2\frac{1}{2} H_2O$.	Found.
H_2O	14.37	14.47

I. 0.4028 grm. of the salt dried at 140° gave 0.2601 grm. K_2SO_4.
II. 0.4120 grm. of the salt dried at 140° gave 0.2665 grm. K_2SO_4.

	Calculated for $K_2C_5H_2SO_6$.	Found. I.	 II.
K_2	29.16	28.99	29.04

Action of Bromine.

We have as yet made but few experiments as to the action of bromine in aqueous solution upon β-sulphopyromucic acid. They have only been sufficient to show that oxidation here follows the same course that it does in the case of other derivatives of pyromucic acid, in which the δ-hydrogen atom is unreplaced. At first products are formed which reduce silver energetically in ammoniacal solution; and only after long warming with an excess of bromine is an acid obtained which resembles in its behavior sulphofumaric acid. Three molecules of bromine gave an acid whose barium salt was very readily soluble in water, and which reduced silver on heating. This reaction will be studied more carefully hereafter, with the hope of isolating the aldehyde acid which is doubtless formed.

Action of Fuming Sulphuric Acid upon βδ-Dibrompyromucic Acid.

By the action of fuming sulphuric acid upon δ-brompyromucic acid, we obtained a sulphonic acid which of necessity contained its sulpho-group either in the β or in the γ position. Analogy left little room for doubt that the acid thus formed was in fact a β-sulphonic acid. It seemed to us not impossible that a γ-sulphonic acid could be formed by the action of fuming sulphuric acid upon βδ-dibrompyromucic acid, which still retains its γ-hydrogen atom. We found, however, that the reaction takes quite a different course, and that no sulphonic acid is formed.

Pure dry βδ-dibrompyromucic acid, melting at 167–168°, was slowly added to several times its weight of fuming sulphuric acid. No visible reaction took place, and after twenty-four hours standing water precipitated the acid apparently quite unchanged. After the lapse of several days decomposition set in, and carbonic dioxide, bromine, hydrobromic acid, and sulphurous dioxide were evolved. So slow was the reaction that two or three weeks were necessary for its completion at ordinary temperatures. When water gave only a slight flocculent precipitate, the bromine was expelled as far as possible with a current of air, and the whole diluted with water. The small quantity of insoluble matter was then removed by filtration, and the aqueous solution thoroughly extracted with ether. The ether left on distillation a white crystalline acid, which, when pressed and dried, melted at 127–128°. The quantity of the acid thus obtained was about half that of the βδ-dibrompyromucic acid taken. The acid dissolved readily in less than its own weight of water, leaving but the slightest turbidity, and on evaporation it crystallized in colorless prisms, which melted at 129–130°.* An analysis showed this substance to be monobrommaleic acid.

0.2235 grm. of the acid dried over sulphuric acid gave 0.2161 grm. AgBr.

Calculated for $C_4H_3BrO_4$.	Found.
41.03	41.15

The melting point and the complete and ready solubility of the crude product showed that monobrommaleic was the only essential constituent. The aqueous solution from which the monobrommaleic acid had been extracted with ether was warmed to expel the ether dissolved, neutralized with baric carbonate, and the filtered solution evaporated. A careful examination of the small amount of barium salt thus obtained failed to show that even a trace of a sulphonic acid had been formed.† This result is in accordance with the results of Hill and Sanger,‡ who found that the γ-hydrogen of the βδ-dibrompyromucic acid could not be replaced by bromine.

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* The melting point of monobrommaleic acid is usually given as 128°, and I have frequently determined it myself without noticing that it varies greatly with the time of heating, as is the case with dibrommaleic acid. How great this variation may be can be seen from the following observations, which I made with this one analyzed sample. The acid in thin-walled capillary tubes was dipped into the bath heated to constant temperature, and the time of melting noted.

Temperature of bath. °	Minutes before melting.
143	0.17
140	0.5
135	0.83
133	1.3
131	1.5
125	4.5
121	8.0

The melting point, 129–130°, given above was the result of two successive attempts to determine it at the ordinary speed. — H. B. H.

† The statement made in a preliminary paper (Berichte d. deutsch. chem. Gesellsch., xviii. 2095), that a sulphonic acid was formed in this reaction, was subsequently proved to be incorrect.

‡ These Proceedings, xxi. 175.

ACTION OF FUMING SULPHURIC ACID UPON TRIBROMPYROMUCIC ACID.

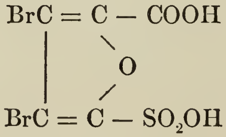
After the experiments just described there could be little doubt as to the action of fuming sulphuric acid upon tribrompyromucic acid. We thought it worth while, however, to make a single experiment in this direction. Tribrompyromucic acid dissolved readily in fuming sulphuric acid, and decomposition quickly ensued at ordinary temperatures, so that the reaction was completed in the course of a day or two. The diluted solution yielded, as the only product of the reaction, dibrommaleic acid, which we recognized by the melting point of its anhydride (114–115°), and by the analysis of its barium salt.

0.5812 grm. of the air-dried salt gave 0.3063 grm. $BaSO_4$.

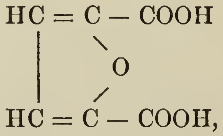
	Calculated for $BaC_4Br_2O_4 . 2H_2O$.	Found.
Ba	31.78	31.98

THEORETICAL CONSIDERATIONS.

The constitution of the various substances described in the preceding pages requires but little discussion. The position of the sulpho-group in the δ-sulphopyromucic acid is established not only by the formation of fumaric acid by its oxidation, but also still more conclusively by its formation in the reduction of βγ-dibrom-δ-sulphopyromucic acid, to which of necessity the formula



must be assigned. The close resemblance in structure of this acid to dehydromucic acid,



is evident, and the formation of δ-nitropyromucic acid from dehydromucic acid as observed by Klinkhardt,* finds its complete parallel in the conversion of this sulphonic acid by the action of nitric acid into $\beta\gamma$-dibrom-δ-nitropyromucic acid and $\alpha\alpha$-dinitro-$\beta\beta$-dibromfurfuran.

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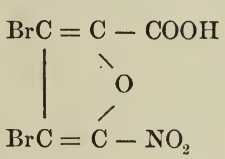
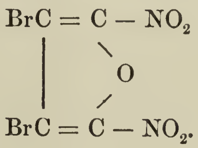
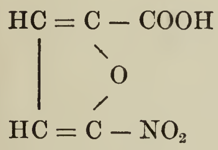
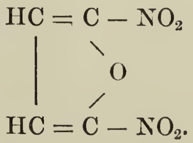
* Journ. pr. Chemie N. F., xxv. 41.



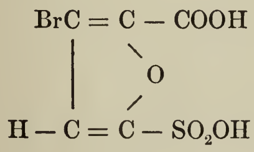


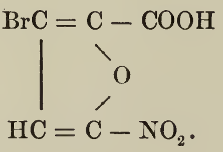
There can be no doubt that the neutral substance formed by the action of fuming nitric acid upon δ-sulphopyromucic acid at the same time with the δ-nitropyromucic acid is $\alpha\alpha$-dinitrofurfuran.





The structure of the β-brom-δ-sulphopyromucic acid is determined by its reduction to δ-sulphopyromucic acid, and by its formation from β-brompyromucic acid, the constitution of which has been established by Hill and Sanger.* The sulphonic acid and the nitro-acid formed from it must be





Concerning the structure of the sulphonic acid formed from δ-brompyromucic acid, it is impossible to draw conclusions equally definite. When we bear in mind, however, the fact that bromine, like sulphuric acid, first replaces the δ-hydrogen atom of the pyromucic acid, and in acting upon the δ-brompyromucic acid thus formed the β-hydrogen alone can further be replaced by bromine, there seems no reasonable doubt that the sulphuric acid in acting upon δ-brompyromucic acid also replaces by the sulpho-group the β-hydrogen atom. This view is still further confirmed by the fact that the γ-hydrogen atom of the $\beta\delta$-dibrompyromucic acid seems incapable of such replacement. If this view be correct, the sulphonic acid in question has the form

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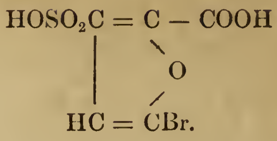
* These Proceedings, xxi. 181.



In any case, the αα-dibromfurfuran-β-sulphonic acid formed from it by the action of bromine has the structure